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Title: Replacement of Environmentally Hazardous Corrosion Protection Paints on the Space Shuttle Main Engine using Wire Arc Sprayed Aluminum.

Abstract: With the advent of new environmental laws restricting hazardous emissions, "environmentally safe" thermal spray coatings are being developed to replace the traditional corrosion protection chromate primers. A wire arc sprayed aluminum coating is being developed for corrosion protection of low pressure liquid hydrogen carrying ducts on the Space Shuttle Main Engine. Currently, this hardware utilizes a chromate primer to provide protection against stress corrosion cracking induced by the cryogenic operating environment. Coating development, adhesion test, corrosion test and cryogenic flexibility test results will be presented. Wire arc sprayed aluminum is proving to provide corrosion protection in aerospace and industrial applications.

Key Words: Corrosion, Wire Arc Spray, Aerospace, Aluminum, Environment

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Abstract

With the advent of new environmental laws restricting hazardous emissions, "environmentally safe" thermal spray coatings are being developed to replace the traditional corrosion protection chromate primers. A wire arc sprayed aluminum coating is being developed for corrosion protection of low pressure liquid hydrogen carrying ducts on the Space Shuttle Main Engine. Currently, this hardware utilizes a chromate primer to provide protection against pitting corrosion leading to stress corrosion cracking induced by the cryogenic operating environment. Coating development, adhesion test, corrosion test, cryogenic flexibility and thermal cycle test results will be presented. Wire arc sprayed aluminum is proving to provide corrosion protection in cryogenic aerospace applications.

CHROMATE PRIMERS are used to provide corrosion protection for aerospace hardware in cryogenic applications. One such application is the Low Pressure Fuel Turbopump (LPFTP) Discharge Duct used on the Space Shuttle Main Engine. The LPFTP Discharge Duct carries liquid hydrogen (-253 °C (-423 °F)) fuel from the Low-Pressure Fuel Turbopump discharge to the inlet of the High-Pressure Fuel Turbopump (see Figure 1). The LPFTP Discharge Duct is fabricated from 21-6-9 CRES (see Table I) which is insulated with polyurethane foam and then nickel plated.

Table I Chemical Composition of 21-6-9 CRES.

Carbon	0.08% Max.
Manganese	8.00% to 10.00%
Chromium	19.00% to 21.50%
Nickel	5.50% to 7.50%
Nitrogen	0.15% to 0.40%
Iron	Balance

These ducts have shown pitting corrosion and stress corrosion cracking after various periods of service. Chloride contamination has been identified as the initiator of the corrosion, although the exact source of the chlorides is not known. Even though 21-6-9 CRES is generally considered corrosion resistant, the corrosion problem is accentuated by the crevice corrosion situation created under the foam insulation (1). To prevent this corrosion, a chromated primer system was qualified and has proven to provide corrosion protection for many years.

However, with increasing health risk and environmental harm due to hazardous materials, many materials are scheduled to be eliminated in the near future. Among the materials to be eliminated, due to excess emissions of hexavalent chromium and volatile organic compounds (VOCs), is the chromate primer system used on the LPFTP Discharge Duct. Other organic coatings have been evaluated for this application with little success, primarily because of difficulty meeting the cryogenic adhesion/flexibility

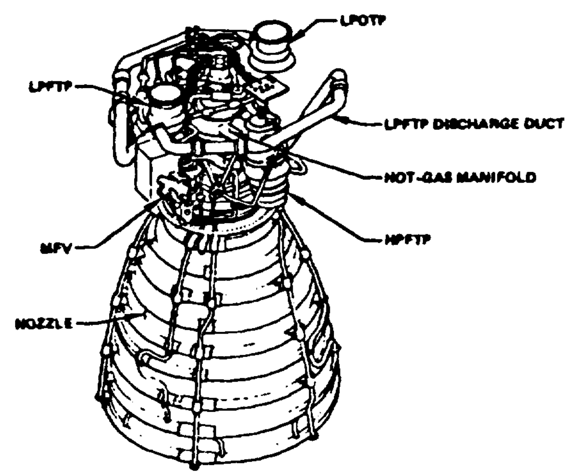


Figure 1 The Space Shuttle Main Engine showing the Low Pressure Fuel Turbopump Discharge Duct.

requirements. Due to the excellent adhesive strength and cryogenic material properties, a wire arc sprayed (WASed) aluminum coating is being developed to replace the chromate primers used in cryogenic applications.

Although thermal sprayed corrosion protection coatings have been used extensively to date, none have been developed for cryogenic applications. The WAS aluminum coating developed meets the stringent adhesion and cryogenic flexibility requirements of the LPFTP Discharge Duct and the coating offers very good corrosion protection for steels and other corrosion prone alloys.

This report presents the details of the coating development program completed including thermal spray parameter development, surface preparation and optimum coating thickness. Corrosion resistance, cryogenic flexibility and adhesion test results are also presented.

Experimental Procedure

Process and Material Selection. The wire arc sprayed aluminum coating was selected based on environmental, cost, availability and performance concerns. Metalized coatings were chosen for their proven corrosion protection capabilities (2) and their typically high adhesive strength. These coatings not only act as an effective barrier coat but because they are more anodic than steel (see Table II), they act as a sacrificial anode and give galvanic protection to the substrate. Thus, corrosion of the substrate will be prevented even where coating coverage may be incomplete or where the coating may be damaged (3). With the addition of a sealant or topcoat, a thermal sprayed coating has long life and is easy to clean and maintain. Also, the sealant does not degrade the cathodic protection.

The wire arc spray process applies metal coatings using metal feedstock in wire form. Two wires serving as the positive and negative electrodes advance to meet in a location in the atomizing gas. A potential is applied to the wires so that an arc is formed at the wire intersection causing the wire tips to melt. Atomizing gas flows across the arc zone propelling molten metal droplets to the substrate (see Figure 2). Because of the high temperatures in the arc zone and the superheating of the molten particles, wire arc spray coatings tend to have excellent adhesion and cohesive strength. Substrate heating however, is significantly lower than most thermal spray processes because there is no flame. In addition, wire arc spray systems are light and portable allowing for on-site application or repair of coatings.

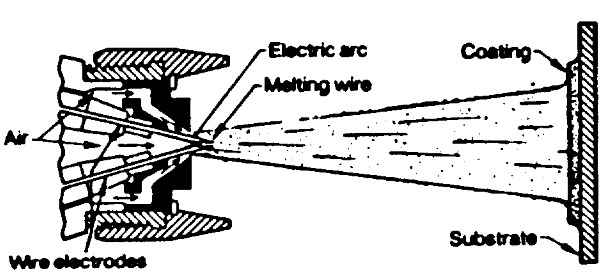


Figure 2 Schematic of the Hobart TAFA wire arc spray gun.

Aluminum and zinc and their alloys are the most commonly used metals for corrosion protection coatings. Zinc, however, was not considered due to it's excessive rate of corrosion (4). Aluminum and aluminum alloys were initially selected based on their electro-chemical potential, good material properties at cryogenic temperatures, low weight and availability.

Preliminary screening of aluminum and two alloys, Al 4043 and Al 5356, coatings was performed in an effort to select one coating for further study. The screening tests consisted of flexibility, adhesion and 30 day salt fog exposure. The best performing coating was selected for further evaluation in cryogenic flexibility, thermal cycle testing and extended salt fog exposure.

Parameter Development. The parameter development process concentrated on the setup of five fundamental parameters that are common with most thermal spray processes. These were:

1) Surface Preparation
2) Atomizing Gas
3) Standoff Distance
4) Power Settings
5) Gun and Part Motion

As with most development programs, it soon became evident that the controllable parameters were not independent of each other. In order to evaluate the affects of parameter changes a "goodness" criteria was developed and used to test each change. This criteria was the coatings performance in a bend test. This test is described in detail in the "Experimental Testing" section later in this paper. The coating passes the test if loss of adhesion or coating cracks do not occur. The test is made more severe by decreasing the bend radius.

Several surface preparation techniques were investigated ranging from grit blasting to a light hand sand. An important factor in the decision was the inspection requirements on the LPFTP Discharge Duct. Periodically the duct is taken out of service and the foam and chromate paint is stripped off so the exterior can be inspected for corrosion pitting and cracking using IVc dye penetrant. If the exterior of the duct had been severely roughened, as with grit blasting, the IVc dye penetrant would show many false indications because of its extreme sensitivity. Our testing proved this to be true so grit blasting was ruled out from the start. A variety of hand sanding techniques were tried with different grit sand paper. From these test, a light hand sand with 320 grit Al_2O_3 sand paper and acetone final clean gave a good surface for coating adhesion and was smooth enough for IVc dye penetrant inspection.

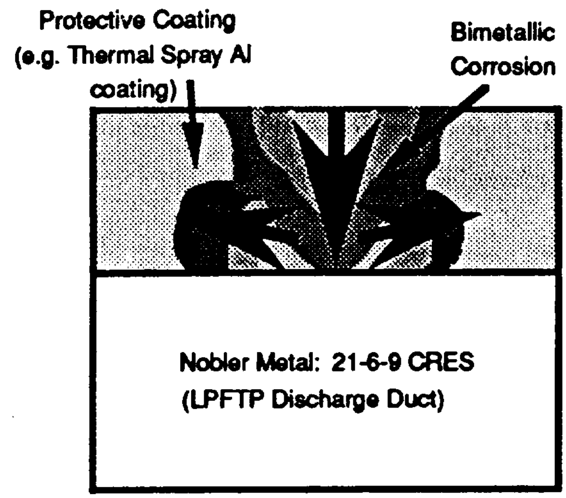
At the beginning of the study, it was assumed that an inert atomizing gas would perform better because of the less likelihood of oxide formation. This turned out to be a false assumption. A variety of atomizing gasses were tried including; argon, 95% Ar - 5% H_2, nitrogen, and air. The different gasses were tested using bend tests to evaluate adhesion and microstructure to determine oxide content and density. Surprisingly using argon, argon-hydrogen and nitrogen as the atomizing gas showed no decrease in oxide content within the microstructure as compared with using

Table II Relative EMF Potentials for Galvanic Corrosion (5)

EMF Potentials for Galvanic Corrosion

	METAL	EMF (V)
Noble End (cathode)	Inconel 625	0.24
	21-6-9 CRES	0.14
	Silver	0.00
	Inconel 718	-0.13
	Nickel 200	-0.14
	Copper	-0.16
	Al Alloy 2024	-0.65
	Al Alloy Tens-50	-0.79
(anode)	Aluminum	-0.80
Base End	Al Alloy 5052	-0.96

Cathodic Protection



- Nobler metal protected from corrosion due to sacrificial anodic coating.

air. Also, using air as the atomizing gas showed a marked increase in bond strength over the other three. This higher bond strength is most noticeable on ferrous substrates, although air seems to generally give higher bond strengths on most metals when spraying aluminum.

Three different standoff distances were evaluated, these being 12 cm (5 in), 18 cm (7 in) and 25 cm (10 in). The 12 cm (5 in) and 25 cm (10 in) distances tended to degrade the microstructure by increasing porosity as compared to 18 cm (7 in). 12 cm (5 in) and 18 cm (7 in) gave similar good results in the bend test, but the 25 cm (10 in) distance showed a marked reduction in coating adhesion. A standoff distance of 18 cm (7 in) gave the best overall results.

The settings for the power input to the wire arc gun are controlled by the power supply and the wire feed rate. The desired voltage is dialed in and the power supply will vary the amperage output needed to maintain that voltage. As the wire feed rate is increased, the amperage output at the power supply will increase to maintain the set voltage. These parameters were not varied much since there is only a narrow operating range for each particular wire material. The voltage is adjusted by running the equipment and varying the voltage until a smooth uniform arc achieved as the wired meet. If the voltage is slightly above or below the optimum point, the wire will pop and spit. The current is set by increasing the wire feed rate to a point just below the speed when wire popping occurs. The final parameters are shown in Table III.

Development of gun motion was done to achieve approximately 25 µm (0.001 in) of deposited material per pass. The gun motion was provided by an X-Y manipulator. The substrate was held stationary and the gun passed back and forth in front of it. After each crossing pass the Y axis moved up or down a specified amount to provide full coverage as the manipulator moved up and down the length of the substrate. It was found that a Y-step of 0.9 cm (0.35 in) after each X-pass gave a uniform coating with consistent thickness. An X-axis traverse velocity of 38 cm/sec (15 in/sec) was found to deposit approximately 25 µm (0.001 in) of material.

Experimental Testing. Adhesion, corrosion resistance, cryogenic flexibility, and thermal cycle tests were performed to further evaluate the aluminum coating for use as a corrosion protection coating in cryogenic applications on flight hardware.

Adhesion and Flexibility. The bend and tape tests were used to evaluate the coating flexibility and bond strength. The bend test was done using a 2.54 cm (1 in) by 15.24 cm (6 in) by 1.27 mm (0.050 in) metal strip coated with the material to be tested. The coupon and coating were bent over a known radius while at room temperature. After bending, the coatings were inspected for signs of cracking or loss of coating adhesion. If the coating passed the bend test then a certified adhesive tape was applied over the coating at the bend area and quickly removed. The coating passed the test if none of the coating material spalled from the substrate. The bend and tape test was made increasingly more severe by decreasing the bend radius.

Initially samples were bent around a 1.27 cm (0.5 in) mandrel as this was the requirement for coatings on the LPFTP discharge duct. As the testing and development proceeded, the procedure included additional bends around a 0.76 cm (0.3 in) mandrel and a 180 degree bend applied by severely bending the sample back on itself and pressing it flat.

Cryogenic Flexibility. The cryogenic flexibility of the coating was evaluated by subjecting samples to a bend test in liquid nitrogen. The coated samples were loaded in a "V" block test fixture submerged in liquid nitrogen. The samples were allowed to stabilize at liquid nitrogen temperatures (-195 °C (-320 °F)) and then bent to the radius of the fixture using a mandrel of 7.11 cm (2.8 in) in diameter. The mandrel size was determined by examining the bend radii of dents in the LPFTP discharge ducts which were damaged by cryo-pumping and selecting the most severe case (the smallest radii) for testing. After warming the samples to ambient temperature, the coatings were examined for evidence of cracking or loss of adhesion.

Salt Fog Exposure. 10 cm (4 in) x 15 cm (6 in) panels were hand sanded and wire arc sprayed with aluminum. Scribes were placed on each sample penetrating the coating and marring the substrate, allowing for evaluation of the cathodic protection capabilities for each material tested. The samples were mounted 6 degrees from the vertical and were placed in a salt fog cabinet with a 5% salt solution conforming to ASTM B-117. The coatings and the substrate of the panels were visually examined after 30, 60, 90 and 120 days of exposure. Coatings were removed from the panels for substrate inspection with a weak caustic soda solution.

Thermal Cycle. A cold flow thermal cycle test was performed using liquid hydrogen (-253 °C (-423 °F)). A 21-6-9 CRES test duct was coated with a WAS aluminum coating (Figures 3 - 4) and then insulated with polyurethane foam. Liquid hydrogen was passed through the duct until the duct wall temperature stabilized at approximately (-253 °C (-423 °F)). That temperature was held for the desired length of time and then allowed to warm up to ambient temperature. Ten 30 minute steady state cycles were performed and one eight hour steady state cycle was performed. After the testing the insulation was removed and the WAS aluminum coating was examined for cracking or loss of adhesion.

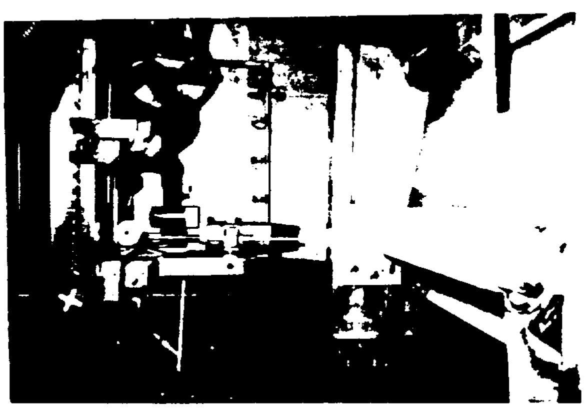


Figure 3 Cold flow test article during wire arc spray process.

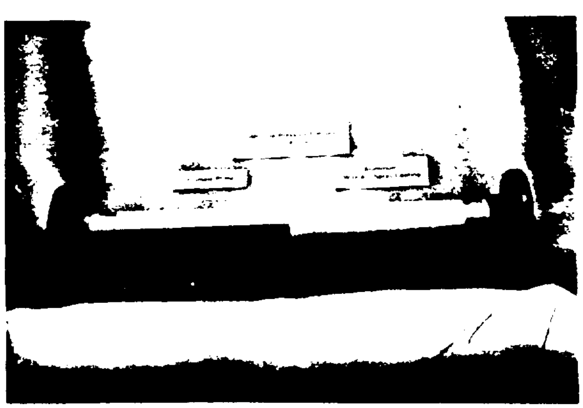


Figure 4. Cold flow test article prior to foam insulation.

Results and Discussion

Material Selection. Pure aluminum, Al 4043 and Al 5356 aluminum alloys were initially screened in an effort to choose one coating for further study. Coatings were screened based on their adhesion, flexibility and corrosion resistance capabilities. The coating's adhesion strength was evaluated quantitatively from the pass or fail bend test starting with 1.27 cm (0.5 in) diameter mandrel and going to a 180 degree bend and tape test. In all cases the pure aluminum coatings performed the best, followed by the Al 5356 coating and lastly the Al 4043 coating.

Each coating was also evaluated after 30 days of salt fog exposure. Coated 21-6-9 CRES panels were scribed through the coating to the base metal to evaluate the cathodic protection provided by each material. After the 30 days of salt fog exposure, the coating and the scribe were visually examined for corrosion. The coating was then removed and the substrate was examined for signs of corrosion. The pure aluminum and the 5356 alloy showed little coating corrosion product and no substrate corrosion was apparent. There was significantly more corrosion product produced from the 4043 alloy and some rust stains were observed on the substrate.

Based on the results of the screening tests, the pure aluminum was chosen for further evaluation. Additional tests included cryogenic bend, extended salt fog exposure up to 120 days, and a thermal cycle cold flow test.

Parameter Development. Micrographs of the aluminum coating (see Figure 5) show the typical splat structure of a wire arc coating. The bond line shows an excellent interface even without a grit blasted surface. The coating also exhibits above average density (greater than

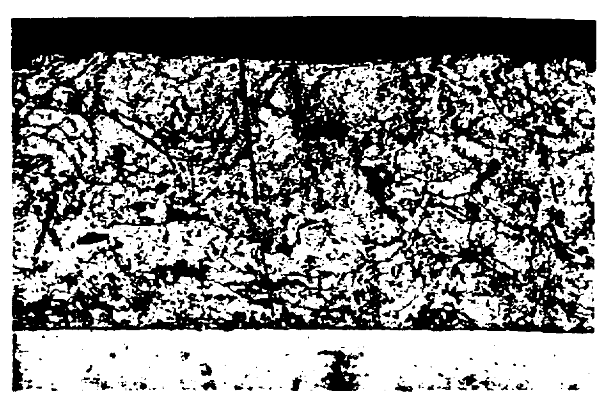


Figure 5 Wire arc sprayed aluminum microstructure deposited on non-grit blast substrate, etched, magnification 200x.

95%) for wire arc and no through porosity, although for galvanic corrosion protection, some through porosity is acceptable. Surprisingly, there are few oxide strings between the splat particles even though air is used as the atomizing gas. Overall, a well adhered and dense wire arc spray coating.

The list of the final processing parameters is shown in Table III. Using these parameters, in conjunction with the Hobart TAFA 8835 Wire Arc Spray System, typical coatings as shown in Figure 5, were repeatably produced.

Table III WAS Aluminum Coat Processing Parameters

Wire Material	01T Al (Hobart TAFA)
Wire Size	1.58 mm (1/16 in) Diameter
Substrate Material	21-6-9 CRES (Nitronic 40)
Surface Preparation	Hand Sand 320 Grit Al_2O_3
Gun Hardware	Green End Cap Long Cross Nozzle
Spray Parameters	
Ionization Gas	Air
Gas Spray Pressure	5.51 Bar (80 psi)
Wire Feed Rate	9.14 cm/sec (3.6 in/sec)
Voltage	28 Volts
Amperage	150 Amps
Spray Distance	18 cm (7 in)
Motion	
Traverse Speed	38 cm/sec (15 in/sec)
Up/Down Step	0.9 cm (0.35 in)

Experimental Testing. The experimental results reported are for samples prepared with the developed parameters shown above. The surface was prepared with a 320 grit hand sand and acetone hand wipe.

Adhesion and Flexibility. The pure aluminum coating passed all bend and tape test (see Figure 6). The Al 5356 alloy passed only the tape and bend test around the 1.27 cm (0.5 in) mandrel. In general, the thinner coatings proved to have better adhesion and cohesive strength. But the pure aluminum coatings up to 0.25 mm (0.010 in) thick were found to pass the all of the bend and tape test, including the 180 degree bend.

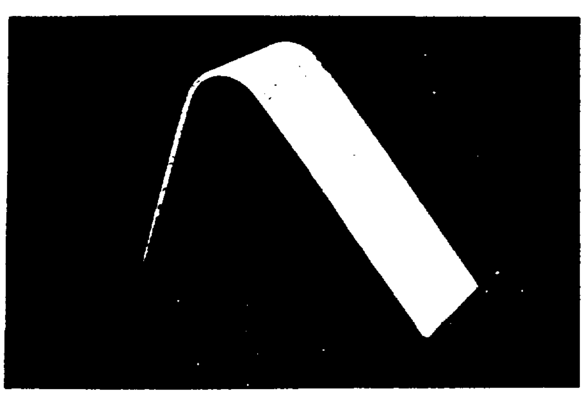


Figure 6 Typical bend test sample coated with wire arc sprayed aluminum (bent around 1.27 cm (0.5 in) mandrel).

Cryogenic Flexibility. Pure aluminum coatings of varied thicknesses, ranging from 0.10 mm (0.004 in) to 0.25 mm (0.010 in) were prepared for the cryogenic bend test. All coatings passed the cryogenic bend test.

Corrosion Resistance. During the initial 30 day test phase, coatings of varied thickness were evaluated. Coating thicknesses of 0.07 mm (0.003 in), 0.18 mm (0.007 in) and 0.25 mm (0.010 in) were tested. Observations of the test panels after 30 days of exposure were:

1. no corrosion of the substrate
2. aluminum oxide formed covering the WASed aluminum coating
3. the thicker coatings tended to blister and loose adhesion
4. the 0.07 mm (0.003 in) and 0.18 mm (0.007 in) coatings remained in satisfactory condition

Since the life of the coating is directly related to the coating thickness, the 0.18 mm (0.007 in) coating, which did not blister or debond, (and was expected to last longer) was chosen for further salt fog testing. Additional panels were prepared and tested for 60, 90 and 120 days. Panels before and after 90 and 120 day salt fog exposure are shown in figures 7-9. As shown, the coating remains intact and there is no corrosion of the substrate. Some exposed base metal can be seen along the edges of the panels and there are some blotchy areas where the coating appears to have thinned. The exposed metal area of the panel increased when exposed for 120 days. After removal of the coating, examination of the substrate revealed no corrosion.

Conclusion

Although wire arc spray coatings have been used in the past for numerous corrosion protection applications, its use in a cryogenic environment has been nonexistent. Rocketdyne's commitment to elimination of hazardous materials on the SSME presented an excellent application for wire arc sprayed aluminum's use in a liquid hydrogen environment. In developing this alternative process for providing corrosion protection for the SSME, a number of innovations were refined.

Parameters were developed that enabled a dense well adhered wire arc sprayed aluminum coating to be applied to both flat and cylindrical 21-6-9 substrates. It was found that using air as the atomizing gas at a high pressure (5.51 bars (80 psi)) gave the best microstructure and bond strength. Using air as the atomizing gas was shown to give higher bonds strength on ferrous substrates than using an inert gas.

The wire arc sprayed aluminum coating was shown to survive cryogenic bend tests on a 7.11 cm (2.8 in) OD mandrel. This achievement is significant in the fact that no other corrosion protection paints, other than the currently used hazardous chromate primer, were able to survive this test.

It was shown that wire arc sprayed pure aluminum provided better corrosion protection on 21-6-9 than the Al 4043 and Al 4043. The wire arc sprayed aluminum proved that it could provide protection for 21-6-9 in 30, 60, 90, and

120 day salt fog test, a significant achievement for any cathodic protection coating.

It was shown that the coating could be sprayed onto representative SSME duct hardware. This cold flow test

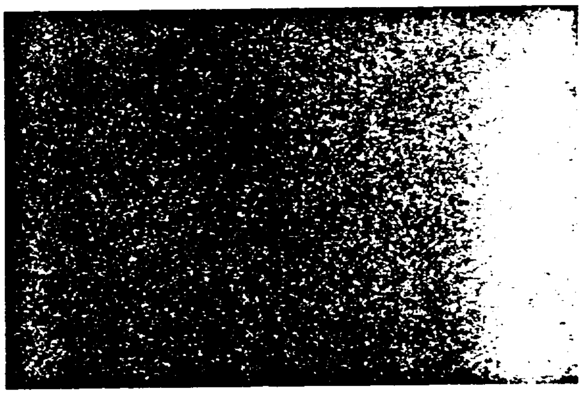


Figure 7 Corrosion test panel wire arc sprayed with aluminum (as-sprayed).

Figure 8 Wire arc sprayed aluminum coating after 90 days salt fog exposure.

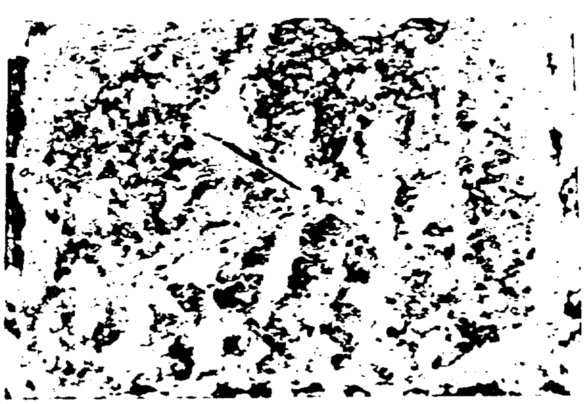


Figure 9 Wire arc sprayed aluminum coating after 120 days salt fog exposure.

specimen was cycled from liquid hydrogen temperatures to ambient repeatably without any degradation in the coating.

In summary, it was shown that wire arc sprayed aluminum can be used to replace environmentally undesirable chromate paints and primers used for corrosion protection of cryogenic hydrogen carrying ducts on the Space Shuttle Main Engine.

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